SECTION 5 WATER CHEMISTRY

by Alan T. Herlihy¹

There are two components to collecting water chemistry information: Collecting samples of stream water to ship to the analytical laboratory, and obtaining *in situ* or stream-side measurements of specific conductance, dissolved oxygen, and temperature. At each stream, teams fill one 4-L container and two-four 60 mL syringes (depending on lab analytes to be measured) with streamwater. These samples are stored in a cooler packed with plastic bags filled with ice and are shipped or driven to the analytical laboratory within 24 hours of collection (see Section 3). The primary purposes of the water samples and the field chemical measurements are to determine:

- Acid-base status
- Trophic condition (nutrient enrichment)
- Chemical Stressors
- Classification of water chemistry type.

Water from the 4-L bulk sample is used to measure the major cations and anions, nutrients, total iron and manganese, turbidity and color. The syringe samples are analyzed for pH, dissolved inorganic carbon, and monomeric aluminum species. Syringes are used to seal off the samples from the atmosphere because the pH, dissolved inorganic carbon (DIC), and aluminum concentrations will all change if the streamwater equilibrates with atmospheric CO₂. Overnight express mail for these samples is required because the syringe samples need to be analyzed, and the 4-L bulk sample needs to be stabilized (by filtration and/or acidification) within a short period of time (72 hours) after collection.

In situ and streamside measurements are made using field meters and recorded on standard data forms. Specific conductance (or conductivity) is a measure of the ability of the water to pass an electrical current which is related to the ionic strength of a solution.

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Dissolved oxygen (DO) is a measure of the amount of oxygen dissolved in solution. In natural waters, minimal concentrations of oxygen are essential for survival of most aquatic organisms. Measures of DO and temperature are used to assess water quality and the potential for healthy aerobic organism populations. Most of the procedures outlined in this section are similar to the ones utilized by the EPA in streams for the National Surface Water Survey (Kaufmann et al., 1988) and have been adapted from the Survey's field operations handbook (U.S. EPA, 1989).

Changes in procedures from Herlihy (1998) and from year 2000 EMAP-WP field operations are summarized in Table 5-1. Activities and procedures presented here are essentially unchanged from those previously published for EMAP-SW (Herlihy, 1998). The volume of the bulk water sample has been reduced from approximately 4 L to approximately 3 L. Procedures for measuring in situ DO and conductivity using a combination oxygen/conductivity/temperature meter are now included. Beginning in 2001, field measurements of dissolved oxygen and conductivity are optional. If field measurements are done, the frequency of QCCS checks of the conductivity meter is reduced. Also, the time of field measurements is recorded.

5.1 SAMPLE COLLECTION

Before leaving the base location, package the sample containers (one 4-L cubitainer and 60 mL syringes) and the stream sample beaker to prevent contamination (see Section 3). Fill out a set of water chemistry sample labels as shown in Figure 5-1. Attach a completed label to the cubitainer and each syringe and cover with clear tape strips as described in Section 3. Make sure the syringe labels do not cover the volume gradations on the syringe. In the field, make sure that the labels all have the same sample ID number (barcode), and that the labels are securely attached.

The procedure to collect a water chemistry sample is described in Table 5-2. The sample is collected from the middle of the stream channel at the X-site, unless no water is present at that location (see Section 4). Throughout the sampling process, it is important to take precautions to avoid contaminating the sample. Rinse all sample containers three times with portions of stream water before filling them with the sample. Many streams have a very low ionic strength and can be contaminated quite easily by perspiration from hands, sneezing, smoking, insect repellent, or other chemicals used when collecting other types of samples. Thus, make sure that none of the water sample contacts your hands before going into the cubitainer. All of the chemical analyses conducted using the syringe samples are

TABLE 5-1. SUMMARY OF CHANGES IN WATER CHEMISTRY PROCEDURES FOR THE WESTERN PILOT STUDY

Changes from Herlihy (1998)

- 1. The volume of bulk water sample is reduced from 4-L to 3-L.
- 2. Procedures for using combination oxygen/conductivity/temperature meters are included.

Changes from Year 2000 Western Pilot Study Activities

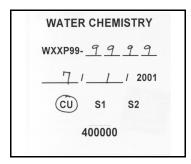
- 1. Dissolved oxygen and conductivity measurements are now optional.
- 2. The frequency of performance evaluation checks for field conductivity meters is reduced from before each field measurement to less frequent checks at base sites or home offices/ laboratories. If used, meters should be subjected to QCCS checks at a minimum frequency of before and after the field season.
- 3. The field form where D.O. and temperature measurements are recorded also has the Channel constraint information and is not on the reverse of the discharge form.
- 4. If field measurements are taken, the time of the measurements is recorded on the field data form..

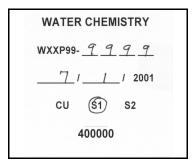
affected by equilibration with atmospheric carbon dioxide; thus, it is essential that no outside air contact the syringe samples during or after collection.

Record the information from the sample label on the Sample Collection Form as shown in Figure 5-2. Note any problems related to possible contamination in the comments section of the form.

5.2 FIELD MEASUREMENTS

Table 5-3 presents the procedures for obtaining field measurement data for the water chemistry indicator. The conductivity and dissolved oxygen meters (if used) are checked in the field using the same procedures as those used at a base location (Section 3). The quality control check sample solution (QCCS) for conductivity is prepared according to directions presented in Section 3. The results of field checks of these meters, the transect where the measurement was made (usually the X-site), as well as the measured values for specific conductance, dissolved oxygen, collection time, and stream temperature, are recorded on the Field Measurement Form as shown in Figure 5-3.





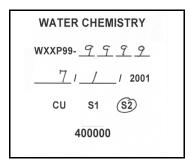


Figure 5-1. Completed sample labels for water chemistry.

If a combination dissolved oxygen/conductivity/temperature meter is being used to determine in situ conditions, the procedure presented in Table 5-4 may be more appropriate to use.

5.3 EQUIPMENT AND SUPPLIES

A list of equipment and supplies required to collect samples and field data for the water chemistry indicator is presented in Figure 5-4. This checklist is similar to the checklist presented in Appendix A, which is used at the base location (Section 3) to ensure that all of the required equipment is brought to the stream. Use this checklist to ensure that equipment and supplies are organized and available at the stream site in order to conduct the activities efficiently.

5.4 LITERATURE CITED

Herlihy, A.T. 1998. Water chemistry. pp. 57-65 IN: J.M. Lazorchak, D.J. Klemm, and D.V. Peck (Eds.). *Environmental Monitoring and Assessment Program-Surface Waters: Field Operations and Methods for Measuring the Ecological Condition of Wadeable Streams*. EPA/620/R-94/004F. U.S. Environmental Protection Agency, Washington, D.C.

TABLE 5-2. SAMPLE COLLECTION PROCEDURES FOR WATER CHEMISTRY

Collect the water samples from the X-site in a flowing portion near the middle of the stream.

- Rinse the 500 mL sample beaker three times with streamwater, Discard the rinse downstream.
- 2. Remove the cubitainer lid and expand the cubitainer by pulling out the sides. **NOTE: DO NOT BLOW into the cubitainers to expand them, this will cause contamination.**
- 3. Fill the beaker with streamwater and slowly pour 30-50 mL into the cubitainer. Cap the cubitainer and rotate it so that the water contacts all the surfaces. Discard the water downstream. Repeat this rinsing procedure two more times.
- 4. Collect additional portions of streamwater with the beaker and portions will have to be Let the weight of the water expand the cubitainer. The first two portions will have to be poured slowly as the cubitainer expands. Fill the cubitainer to at least three-fourths of its maximum volume. Rinse the cubitainer lid with streamwater. Eliminate any air space from the cubitainer, and cap it tightly. Make sure the cap is tightly sealed and not on at an angle.
- 5. Place the cubitainer in a cooler (on ice or streamwater) and shut the lid. If a cooler is not available, place the cubitainer in an opaque garbage bag and immerse it in the stream.
- 6. Submerge a 60-mL syringe halfway into the stream and withdraw a 15-20 mL aliquot. Pull the plunger to its maximum extension and shake the syringe so the water contacts all surfaces. Point the syringe downstream and discard the water by depressing the plunger. Repeat this rinsing procedure two more times.
- 7. Submerge the syringe into the stream again and **slowly** fill the syringe with a fresh sample. Try not to get any air bubbles in the syringe. If more than 1-2 tiny bubbles are present, discard the sample and draw another one.
- 8. Invert the syringe (tip pointing up), and cap it with a syringe valve. Tap the syringe lightly to detach any trapped air bubbles. With the valve open, expel the air bubbles and a small volume of water, leaving between 50 and 60 mL of sample in the syringe. Close the syringe valve. If any air bubbles were drawn into the syringe during this process, discard the sample and fill the syringe again (Step 7).
- 9. Repeat Steps 6 through 8 with a second syringe. Place the syringes together in the cooler or in the streamwater with the cubitainer.
- 10. Record the barcode number (Sample ID) on the Sample Collection Form along with the pertinent stream information (stream name, ID, date, etc.). Note anything that could influence sample chemistry (heavy rain, potential contaminants) in the Comments section. If the sample was collected at the X-site, record an "X" in the "STATION COLLECTED" field. If you had to move to another part of the reach to collect the sample, place the letter of the nearest transect in the "STATION COLLECTED" field. Record more detailed reasons and/or information in the Comments section.
- 11. After carrying the samples out to the vehicles, place the cubitainer and syringes in a cooler and surround with 1 gallon self-sealing plastic bags filled with ice.

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Figure 5-2. Sample Collection Form, showing data recorded for water chemistry samples.

TABLE 5-3. PROCEDURES FOR STREAMSIDE AND IN SITU CHEMISTRY MEASUREMENTS

Specific Conductance

NOTE: Beginning in 2001, streamside and in situ chemistry measurements are optional.

- 1. Check the batteries and electronic functions (e.g., zero, "red line") of the conductivity meter as instructed by the operating manual.
- 2. If you haven't tested the meter at a base location recently, insert the probe into the "RINSE" container of the quality control check sample (QCCS) and swirl for 3 to 5 seconds. Remove the probe, shake it off gently, transfer it to the "TEST" container of QCCS, and let it stabilize for 20 seconds.

If the measured conductivity is not within 10% or 10 μ S/cm of theoretical value, repeat the measurement process. If the value is still unacceptable, do not use the meter until it can be troubleshooted and repaired.

3. Submerge the probe in and area of flowing water near the middle of the channel at the same location where the water chemistry sample is collected. Record the measured conductivity and any pertinent data comments about the measurement on the Field Measurement Form.

Dissolved Oxygen and Temperature

- 1. Inspect the probe for outward signs of fouling and for an intact membrane. Do not touch the electrodes inside the probe with any object. Always keep the probe moist by keeping it inside its calibration chamber.
- Check the batteries and electronic functions of the meter as described in the operating manual.
- Calibrate the oxygen probe in water-saturated air as described in the operating manual. Allow
 at least 15 minutes for the probe to equilibrate before attempting to calibrate. Try to perform
 the calibration as close to stream temperature as possible (not air temperature) by using
 stream water to fill the calibration chamber prior to equilibration.
- 3. After the calibration, submerge the probe in midstream at mid-depth at the same location where the water chemistry sample is collected. Face the membrane of the probe upstream, and allow the probe to equilibrate. Record the measured DO and stream temperature on the Field Measurement Form. Record the time the DO and temperature measurement was made in 24 hour units (e.g. 14:23) on the field form. If the DO meter is not functioning, measure the stream temperature with a field thermometer and record the reading on the Field Measurement Form along with any pertinent data comments.

NOTE: Older model dissolved oxygen probes require a continuous movement of water (0.3 to 0.5 m/s) across the probe to provide accurate measurements. If the velocity of the stream is appreciably less than that, jiggle the probe in the water as you are taking the measurement.

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	TIME OF DAY: 1,1:2,5								
	C	ANNEL CONSTRAINT							
HAI	NNEL PATTERN (Check One)								
X	One channel								
	Anastomosing (complex) channel - (Relatively long major and minor channels branching and rejoining.)								
	Braided channel - (Multiple short channels br numerous mid-channel bars.)	anching and rejoining - mai	inly one channe	el broken up by					
CHAI	NNEL CONSTRAINT (Check One)								
	Channel very constrained in V-shaped valle new channel during flood)	y (i.e. it is very unlikely to s	spread out over	valley or erode a					
	Channel is in Broad Valley but channel move flows do not commonly spread over valley floor			ned by Incision (Flood					
	Channel is in Narrow Valley but is not very valley floor (< ~10 x bankfull width)	constrained, but limited in	movement by	relatively narrow					
X	Channel is Unconstrained in Broad Valley (spread out over flood plain, or easily cut new or		f-channel areas	s and side channels,					
CON	STRAINING FEATURES (Check One)								
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	Hillslope (i.e. channel constrained in narrow \	-shaped valley)							
	Terrace (i.e. channel is constrained by its own	incision into river/stream g	ravel/soil depo	sits)					
	Human Bank Alterations (i.e. constrained by	rip-rap, landfill, dike, road,	etc.)						
×	No constraining features								
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Figure 5-3. Channel Constraint and Field Measurement Form, showing data recorded for water chemistry.

TABLE 5-4. PROCEDURES FOR IN SITU MEASUREMENTS OF DISSOLVED OXYGEN, CONDUCTIVITY, AND TEMPERATURE USING A MULTI-FUNCTION METER^a

NOTE: Beginning in 2001, field conductivity measurements are optional.

Conductivity QCCS check (no longer required at every site):

- 5. Check the probe for fouling, intact and unwrinkled oxygen membrane, and bubble behind the membrane. Replace the electrolyte solution and membrane cap assembly if necessary.
- 6. Turn the meter on and allow the self-test sequence to finish (approx. 15 seconds).
- 7. Use the MODE key to display "temperature compensated" conductivity (The "°C" symbol on the display will be flashing).
- 8. Swirl the conductivity probe for 3-5 seconds in a 250-mL bottle containing the daily QCCS solution labeled "RINSE".
- 9. Transfer the probe from the "RINSE" bottle to a second 250-mL bottle of QCCS labeled "TEST". Let stabilize for 20 seconds.
- If the measured value of the QCCS is within ±10% or ±10 μS/cm of the theoretical value (whichever is greater at the theoretical value), rinse the probe in deionized water and proceed to Step 8.

If the measured value of the QCCS is not within $\pm 10\%$ or $\pm 10~\mu$ S/cm of theoretical value, repeat Steps 4 through 6.

11. If the value is still unacceptable, replace the QCCS in both the "Rinse" and "Test" bottles and repeat the measurement process.

If the measured value is still not acceptable, clean the conductivity probe as described in the manual, check the batteries, and repeat Steps 1 through 6.

If the measured value is still unacceptable, do not make any conductivity measurements. Note problems in the comments section of the field measurement form.

Dissolved oxygen calibration:

- 12. Check the calibration chamber and fill it with stream water to dampen the sponge and get the chamber temperature as close to stream temperature as possible. Drain the chamber and insert the probe into the chamber.
- 13. Press the MODE key until the dissolved oxygen reading inside the chamber is displayed in mg/L. Allow approximately 15 minutes for the readings to stabilize (i.e., a change of < 0.02 mg/L over a 1-minute period).

(Continued)

^a For use with YSI Models 85 and 95. Modified from YSI Incorporated. 1986. *Model 85 Handheld Oxygen, Conductivity, Salinity, and Temperature System Operations Manual.* YSI Incorporated, Yellow Springs, OH.

TABLE 5-4 (continued)

Dissolved oxygen calibration (cont.):

- 14. Press the UP ARROW and DOWN ARROW keys simultaneously to enter calibration mode.
- 15. Obtain the approximate local altitude from either the site dossier or from a topographic map. Use the UP ARROW or DOWN ARROW key to enter the local altitude [to the nearest 100 feet (e.g., "15" equals 1500 ft)]. After the correct altitude is displayed, press the ENTER button.
- 16. In the lower part of the display, "CAL" should appear along with the theoretical value based on temperature and altitude.
- 17. Once the actual value displayed is stable for 10 seconds, press the ENTER button to save the calibration. **NOTE: make sure the display says "SAVE"**. Do not turn the meter off after saving the calibration.

In situ measurements:

- 18. Remove the probe from the calibration chamber and hold it in mid-channel and mid-depth at the X-site. Press the MODE button to cycle the display to DO in mg/L. Face the probe upstream and/or jiggle the probe up and down to ensure a continuous movement of water across the membrane surface. Unstable and inaccurate measurements will result if the flow of water across the membrane is < 0.1 m/s.
- 19. Wait at least 1 minute for the displayed readings to stabilize, and record the DO value and stream temperature on the Field Measurement Form.
- 20. Press the MODE button to cycle the display to specific conductance (the "°C" symbol will flash). Record the displayed conductivity value in μ S/cm on the Field Measurement Form. NOTE: If the conductivity is high (> 999 μ S/cm), the display will convert from μ S/cm to mS/cm. Be sure to check the units indicated on the display. If mS/cm are displayed, multiply the value by 1000 to convert it to μ S/cm before recording it on the data form (e.g., 9 mS/cm would be recorded as 9000 μ S/cm). Extremely low values (< 10) are likely to be in mS/cm in most streams sampled in the Western Pilot Study.
- 21. After completing all in situ measurements, rinse the probe with deionized water and store in the calibration chamber. Be sure to keep the sponge in the chamber moist at all times.

^a For use with YSI Model 85 or equivalent. Modified from YSI Incorporated. 1986. *Model 85 Handheld Oxygen, Conductivity, Salinity, and Temperature System Operations Manual.* YSI Incorporated, Yellow Springs, OH.

EQUIPMENT AND SUPPLIES FOR WATER CHEMISTRY

QTY.	Item	
1	Dissolved oxygen/Temperature meter with probe	
1	DO repair kit containing additional membranes and probe filling solution	
1	Conductivity meter with probe	
1	500-mL plastic bottle of conductivity QCCS labeled "Rinse" (in plastic bag)	
1	500-mL plastic bottle of conductivity QCCS labeled "Test" (in plastic bag)	
1	Field thermometer	
1	500 mL plastic beaker with handle (in clean plastic bag)	
1	4-L cubitainer with completed sample label attached (in clean plastic bag)	
2-4	60 mL plastic syringes (with Luer type tip) with completed sample labels attached	
1	Plastic container with snap-on lid to hold filled syringes	
2-4	Syringe valves (Mininert® with Luer type adapter, or equivalent, available from a chromatography supply company)	
1	Cooler with 4 to 6 plastic bags (1-gal) of ice OR a medium or large opaque garbage bag to store the water sample at streamside	
1	Sample Collection From	
1	Field Measurement Form	
	Soft-lead pencils for filling out field data forms	
	Fine-tipped indelible markers for filling out labels	
1 сору	Field operations and methods manual	
1 set	Laminated sheets of procedure tables and/or quick reference guides for water chemistry	

Figure 5-4. Checklist of equipment and supplies for water chemistry.

- Kaufmann, P., A. Herlihy, J. Elwood, M. Mitch, S. Overton, M. Sale, J. Messer, K. Reckhow, K. Cougan, D. Peck, J. Coe, A. Kinney, S. Christie, D. Brown, C. Hagley, and Y. Jager. 1988. Chemical Characteristics of Streams in the Mid-Atlantic and Southeastern United States. Volume I: Population Descriptions and Physico-Chemical Relationships. EPA 600/3-88/021a. U.S. Environmental Protection Agency, Washington, D.C.
- U.S. EPA. 1989. Handbook of Methods for Acid Deposition Studies: Field Operations for Surface Water Chemistry. EPA 600/4-89/020. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C.

NOTES